Decoupled Direct Method for Sensitivity Analysis in Combustion Kinetics

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SUMMARY

An efficient, decoupled direct method for calculating the first order sensitivity coefficients of homogeneous, batch combustion kinetic rate equations is presented. In this method the ordinary differential equations for the sensitivity coefficients are solved separately from, but sequentially with, those describing the combustion chemistry. The ordinary differential equations for the thermochemical variables are solved using an efficient, implicit method (LSODE) that automatically selects the steplength and order for each solution step. The solution procedure for the sensitivity coefficients maintains accuracy and stability by using exactly the same steplengths and numerical approximations. The method computes sensitivity coefficients with respect to any combination of the initial values of the thermochemical variables and the three rate constant parameters for the chemical reactions. The method is illustrated by application to several simple problems and, where possible, comparisons are made with exact solutions and those obtained by other techniques.

INTRODUCTION

The modeling of a homogeneous, batch combustion system requires the solution of first order ordinary differential equations (ODE's) for thermochemical variables such as composition, temperature, and density. The chemistry is represented by a system of NR simultaneous reactions among NS different species. All chemical reactions considered in this work are gas-phase elementary reactions. The jth chemical reaction can be written in the general form

$$\sum_{i=1}^{NS} v_{ij}' X_i \underset{k_{-j}}{\overset{k_j}{\rightleftharpoons}} \sum_{i=1}^{NS} v_{ij}'' X_i \quad ; \quad j = 1, NR \tag{1}$$
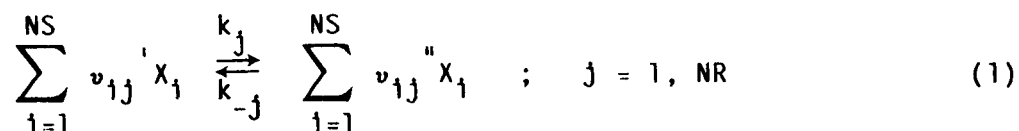
where v_{ij}' and v_{ij}'' are the stoichiometric coefficients of species i (with chemical symbol X_i) in reaction j as a reactant and as a product, respectively.

The time rate of change of species i can be written as (refs. 1 and 2)

$$\frac{d\sigma_i}{dt} = f_i(\{\sigma_k\}, T, \rho) \quad ; \quad i, k = 1, NS \tag{2}$$

where σ_i is the mole number of species i (i.e., mole i/g mixture), t the time, T the temperature, and ρ the mixture mass density. The net rate of formation (f_i) of species i due to all forward and reverse reactions is given by

$$f_1 = \rho^{-1} \sum_{j=1}^{NR} (v_{1j}{}' - v_{1j}{}'')(R_{-j} - R_j) \qquad (3)$$

where the molar forward (R_j) and reverse (R_{-j}) rates per unit volume for reaction j are given by

$$R_j = k_j \prod_{q=1}^{NS} (\rho\sigma_q)^{v_{qj}{}'} \qquad (4)$$

$$R_{-j} = k_{-j} \prod_{q=1}^{NS} (\rho\sigma_q)^{v_{qj}{}''} \qquad (5)$$

The forward rate constant (k_j) is given by the modified Arrhenius expression

$$k_j = A_j T^{n_j} \exp(-E_j/RT) \qquad (6)$$

where A_j, n_j, and E_j are constants and R is the universal gas constant. Each reaction may be either reversible (bidirectional) or irreversible (uni-directional). For reversible reactions the reverse rate constants (k_{-j}) are calculated from k_j and the concentration equilibrium constants (K_j) using the principle of detailed balancing (ref. 3)

$$k_{-j} = k_j/K_j \qquad (7)$$

where K_j is a function of temperature alone. Two different types of batch reaction problems can be identified: constant and variable density. For a variable density problem, the pressure-versus-time profile is given and the ODE's for temperature and density take the form (ref. 2)

$$\frac{dT}{dt} = T\left(\frac{\gamma - 1}{\gamma} \frac{1}{p} \frac{dp}{dt} - B - D\right) \qquad (8)$$

and

$$\frac{d\rho}{dt} = \rho\left(\frac{1}{\gamma p} \frac{dp}{dt} - A + D\right) \qquad (9)$$

where p is the absolute pressure and γ, A, B, and D are given by

$$\gamma = c_p/(c_p - R/M_w) \qquad (10)$$

$$c_p = \sum_{i=1}^{NS} \sigma_i c_{p,i} \qquad (11)$$

$$M_w = 1 \bigg/ \sum_{i=1}^{NS} \sigma_i \qquad (12)$$

2

$$A = M_w \sum_{i=1}^{NS} f_i \qquad \qquad B \tag{13}$$

$$B = \frac{M_w}{RT} \left(\frac{\gamma - 1}{\gamma} \right) \sum_{i=1}^{NS} h_i f_i \tag{14}$$

$$D = \frac{M_w}{RT} Q \left(\frac{\gamma - 1}{\gamma} \right) \tag{15}$$

In these equations h_i and $c_{p,i}$ are the molar specific enthalpy and constant-pressure molar specific heat, respectively, of species i, c_p the mixture specific heat, γ the mixture specific heat ratio, M_w the mixture mean molar mass, and Q the heat loss rate per unit mass of mixture. The thermodynamic properties h_i and $c_{p,i}$ are functions of temperature alone and are computed by using polynomial equations (ref. 2). A can be described as a species production function, and B and D are enthalpy production and loss functions, respectively.

For constant density problems the temperature ODE becomes (ref. 2)

$$\frac{dT}{dt} = T \left[(\gamma - 1)A - B - \gamma D \right] \tag{16}$$

and the pressure is obtained from the ideal gas law

$$p = \rho RT / M_w \tag{17}$$

The problem is to determine the thermochemical variables at the end of a prescribed time interval, given the initial conditions and the chemical reaction mechanism.

The use of classical methods such as the explicit Runge-Kutta and Adams methods to solve the ODE's arising in combustion chemistry results in prohibitive amounts of computer time. This is due to the extremely small steplengths required by these methods due to the "stiffness" exhibited by the ODE's (refs. 1, 4, and 5). The phenomenon of stiffness in chemical kinetic rate equations was first recognized by Curtiss and Hirschfelder (ref. 6) who developed a simple backward differentiation method for handling such equations. Since then, many approaches have been proposed for stiff ODE's in general (refs. 7 to 12), and chemical kinetic rate equations in particular (refs. 1, 2, and 10 to 20). In several recent publications (refs. 1, 5, 21, and 22) the accuracy and efficiency of many techniques for the solution of stiff ODE's arising in combustion chemistry have been examined. These studies showed that the packaged code LSODE (ref. 23) is at present the most efficient and accurate algorithm for batch combustion chemistry problems. This code has therefore been adopted in the present work.

In addition to solving the ODE's for the thermochemical variables, it is often necessary to know how sensitive the solution is to the initial conditions and the chemical reaction mechanism parameters. Such a need arises in the development of reaction mechanisms from experimental data (ref. 24). The rate constants are often not well known and in general, the experimental data are

not sufficiently detailed to accurately estimate the rate constant parameters. Sensitivity analysis helps to determine the effects of uncertainties in the rate constant parameters and the initial conditions on the solution, and to identify which variables are sensitive to which parameters. The analysis helps identify unimportant elementary reactions which can be discarded, thereby simplifying the mechanism and hence the problem. At the same time, reactions that need additional experimental study can be identified. Sensitivity analysis helps also in the understanding of complex reaction mechanisms by showing which parts of the mechanism are important for a given problem.

Another motivation for sensitivity analysis is the increased interest in the numerical simulation of multidimensional chemically reacting flows. The coupling of realistic chemical reaction mechanisms with multidimensional flow calculations results in prohibitive amounts of computer time. Sensitivity analysis can help reduce the reaction mechanism by identifying those reactions that are important in computing the variables of interest.

The simplest method for estimating the effect of uncertainties in any parameter is to run the simulation program with two different values of the parameter. Although such a "brute force" method has been used successfully (refs. 25 and 26), it can become very expensive when the number of parameters is large. Many methods (refs. 27 to 39) have been proposed for a more elegant and less expensive sensitivity analysis. The commonly used methods include the direct method (DM) (ref. 27), the Fourier amplitude sensitivity test (FAST) method (ref. 28), the Green's function method (GFM) (refs. 29 and 30) and its variants (refs. 32 and 33), the analytically integrated Magnus modification of the Green's function method (GFM/AIM) (refs. 30 and 34), and the decoupled direct method (DDM) (refs. 37 to 39). For stiff problems of the type examined in the present work, the DDM has shown greater efficiency and stability, with equal or better accuracy than the GFM and the GFM/AIM methods (ref. 37). Advantages of the DDM method over other methods are discussed by Dunker (ref. 37).

Dunker (ref. 40) has recently developed a very efficient computer program CHEMDDM which couples the DDM method for sensitivity analysis with the code LSODE for solution of the model equations. However, the code is restricted to constant density and constant temperature problems. This restriction to constant temperature problems appears to be a common feature among all sensitivity codes developed to date. However, combustion kinetics is characterized by a narrow region of rapidly varying temperature. There is therefore a need to incorporate sensitivity computations into a general kinetics code for nonisothermal problems. In the present work, the DDM method developed by Dunker (refs. 37 and 40) is extended to calculate the first order sensitivity coefficients $\partial y_i/\partial \alpha$, where y_i is the ith thermochemical variable and α is a parameter of interest (either a rate constant parameter or an initial value), for combustion (i.e., nonisothermal) kinetic rate equations.

DECOUPLED DIRECT METHOD

The ODE's for batch combustion chemistry presented in the previous section can be generalized as

$$\dot{\underline{y}} = \frac{d\underline{y}}{dt} = \underline{f}\left(\underline{y}, \underline{A}, \underline{n}, \underline{E}, Q, p, \frac{dp}{dt}\right)$$

$$\underline{y}(t = 0) = \underline{y}_0 \tag{18}$$

where $\underline{y}$ is the solution vector with $NS + 2$ components ($\sigma_i; i=1,NS$, T, ρ) and $\underline{A}$, $\underline{n}$, and $\underline{E}$ are constant vectors (containing the rate constant parameters, eq. 6), each of which has NR components.

At present, the most efficient method for solving eq. (18) is the backward difference formula (BDF) included in the packaged code LSODE (ref. 1). This variable-step, variable-order method computes approximations $\underline{Y}_n$ [$= \underline{Y}(t_n)$] to the exact solution $\underline{y}(t_n)$ using linear multistep formulas of the type

$$\underline{Y}_n = \sum_{\ell=1}^{q_n} \alpha_\ell \underline{Y}_{n-\ell} + h_n \beta_0 \underline{\dot{Y}}_n \tag{19}$$

where $h_n (= t_n - t_{n-1})$ is the stepsize, q_n is the order of the numerical approximation, $\underline{\dot{Y}}_n [= \underline{f}(\underline{Y}_n, \dots)]$ is the approximation of the exact derivative $\underline{\dot{y}}(t_n)[= \underline{f}(\underline{y}(t_n), \dots)]$, and the α's and β_0 are coefficients associated with the order q_n.

A variety of iteration techniques is included in LSODE to solve equation (19). For combustion kinetics problems the modified Newton iteration procedure is the most efficient (ref. 1) and is given by

$$(I - h_n\beta_0 J)\left(\underline{Y}_n^{(m+1)} - \underline{Y}_n^{(m)}\right) = \sum_{\ell=1}^{q_n} \alpha_\ell \underline{Y}_{n-\ell} + h_n\beta_0 \underline{\dot{Y}}_n^{(m)} - \underline{Y}_n^{(m)} \tag{20}$$

where I is the identity matrix, J the Jacobian matrix with element $J_{ij} = \partial \dot{Y}_i/\partial Y_j$, the superscripts (m) and (m+1) denote the iteration numbers, and $\underline{\dot{Y}}_n^{(m)} = \underline{f}(\underline{Y}_n^{(m)}, \dots)$. For each solution step the code automatically selects the stepsize and order to minimize the computational work while keeping the estimated local error within a user-specified error tolerance.

The difference equation for the first-order sensitivity coefficient $\underline{S}_{j,n}\left[= \underline{S}_j(t_n) = (\partial \underline{Y}/\partial n_j)_{t_n}\right]$ where n_j is an initial value or a rate constant parameter, can be obtained by differentiating equation (19) with respect to n_j. The difference equation can also be derived by first differentiating equation (18) with respect to n_j and then applying the BDF to the resulting equation. This gives

$$(I - h_n\beta_0 J)\underline{S}_{j,n} = \sum_{\ell=1}^{q_n} \alpha_\ell \underline{S}_{j,n-\ell} + h_n\beta_0 \frac{\partial \underline{Y}_n}{\partial n_j} \tag{21}$$

where $\partial \underline{\dot{Y}}_n/\partial n_j$ accounts for any explicit dependence of $\underline{\dot{Y}}_n$ on n_j. When n_j is an initial value this term vanishes, and when n_j is a rate constant parameter, it can be obtained from equation (18). The initial value

5

of S_j is the jth column of the identity matrix if n_j is the jth element of y_0. If, however, n_j is a rate constant parameter, $S_j(t = 0)$ is equal to the null vector.

Equations (20) and (21) show the similarity between the model and sensitivity equations. The DDM method exploits this similarity by alternating the solution of equation (19) with that of equation (21). More specifically, the solution procedure is as follows. For any step the solution Y is advanced from t_{n-1} to t_n using a standard predictor and the corrector formula equation (20). The solution Y_n at the new time step is then used in equation (21) to update the sensitivity coefficients. The latter process does not require either a predictor or an iterative procedure. In solving equation (21) for the sensitivity coefficients the method uses exactly the same stepsize and order as those used for equation (19). This implies that the error control in the solution of equation (21) is determined by the error control in the solution of equation (19). As discussed in Dunker (ref. 37) the sensitivity coefficients calculated from equation (21) are the exact sensitivity of Y with respect to n_j, apart from computer roundoff errors.

At each solution step, equation (21) must be solved as many times as the number of parameters with respect to which the solution sensitivity is required. However, since the matrix $(I - h_n \beta_0 J)$ is independent of the sensitivity solutions, it has to be LU-decomposed only once, irrespective of the number of sensitivity parameters. Hence, although the calculation of the sensitivities with respect to the first parameter may require considerable work to form the iteration matrix, perform its LU-decomposition, and solve equation (21), the evaluation of the sensitivity coefficients with respect to the second and subsequent parameters is significantly less expensive.

To reduce the computational work associated with the calculation and decomposition of the iteration matrix $(I - h_n \beta_0 J)$ in equation (20), this matrix is not updated at every iteration in LSODE. For additional savings it is updated only when the solution to equation (20) does not converge. Hence the iteration matrix is only accurate enough for the iterations to converge and the same matrix may be used over many steps. However, to maintain accuracy in the computed S_j, the matrix in equation (21) must be recomputed at every time step unless J changes slowly (refs. 37 and 39). The updating of this matrix at every time step obviates the need to iterate for S_j and specify separate error tolerances for the sensitivity calculations. Notice that because the same Jacobian matrix J is required in both equations (20) and (21) no additional programming is required by the DDM method for either the calculation of J or the LU-decomposition of the matrix $(I - h_n \beta_0 J)$ in equation (21).

ILLUSTRATIVE EXAMPLES

The DDM method of sensitivity analysis together with a modified version of the packaged code LSODE (ref. 23) were incorporated into an existing general chemical kinetics computer code GCKP84 (ref. 2). The sensitivity subroutines were adapted from the code CHEMDDM (ref. 40). The new general kinetics code GCKP87 (ref. 41) has been designed to treat a variety of reaction problems including sensitivity analysis of batch combustion kinetics equations. At the user's option the code computes the first order sensitivity coefficients $\partial y_i / \partial n_j$ where y_i is any dependent variable, the species mole numbers,

temperature, density, and pressure. The n_j's are the input parameter values. This includes the initial values of the species mole numbers, temperature and density, as well as the values of the rate constant parameters A_j, n_j, and E_j for the jth reaction (eq. 6). The code does not compute the coefficient $\partial y_i / \partial k_j$ used in the constant temperature computations of other investigators, because the rate constant k_j is a function of the temperature (eq. 6). The code GCKP87 also computes the sensitivity coefficients of the temporal derivatives of the dependent variables $\partial \dot{y}_i / \partial n_j$ for all the y_i's and n_j's defined above.

A preliminary version of GCKP87 has been tested extensively on a variety of problems to ensure its accuracy and efficiency (ref. 42). To test the sensitivity computations many problems have been examined (ref. 41), three of which are presented below for illustrative purposes. All calculations were performed in double precision on the NASA Lewis Research Center's IBM 370/3033 computer.

Test problem 1, taken from Dunker (ref. 37), describes the pyrolysis of ethane at a temperature of 923 K. This constant temperature, constant density problem consists of 5 irreversible reactions among 7 species. The reaction mechanism and rate constants (at $T = 923$ K) are given in table I, together with the initial conditions. Although the mechanism is quite small this problem is very stiff and other direct methods have produced inaccurate results (ref. 37). Because this is a constant temperature problem the rate constants k_j (eq. 6) are time invariant. Therefore it is only necessary to compute sensitivity coefficients with respect to k_j itself and not with respect to the individual rate constant parameters A_j, n_j, and E_j. This problem was selected as a test for the modifications made to the sensitivity routines adapted from CHEMDDM (ref. 40) to ensure that Dunker's results (ref. 37) could be duplicated.

Normalized sensitivity coefficients

$$\frac{k_j}{\sigma_i} \frac{\partial \sigma_i}{\partial k_j} = \frac{\partial \ln \sigma_i}{\partial \ln k_j}$$

calculated at two different times by the codes GCKP87 and CHEMDDM are given in table II, together with the results obtained by Dunker (ref. 37). All sensitivity coefficients presented in this table are with respect to the rate constant k_1. To generate these coefficients with the code GCKP87, sensitivity with respect to the preexponential constant (A_j in eq. 6) is specified. For constant temperature problems the normalized sensitivity coefficients with respect to A_j are identically equal to the normalized sensitivity coefficients with respect to k_j. To enable accuracy and efficiency comparisons, both GCKP87 and CHEMDDM were run with the same values for the local error tolerance parameters required by LSODE. The values specified for these parameters were the same as those used by Dunker (ref. 37): 10^{-6} for the local relative error tolerance (RTOL) and 10^{-8} for the local absolute error tolerance (ATOL) for all variables.

The agreement between the two codes is excellent at both 1 and 20 sec, thereby confirming the reliability of the code GCKP87. Comparisons of the computational work required by the two codes showed GCKP87 to be significantly

more efficient than CHEMDDM. For 2 output stations (1 and 20 sec), GCKP87 required 95 steps with 138 functional and 21 Jacobian matrix evaluations to complete the problem, whereas CHEMDDM required 140 steps with 193 functional and 28 Jacobian matrix evaluations. To solve for the composition and sensitivity coefficients of all species with respect to all initial values and all rate constants, GCKP87 required approximately 0.65 sec CPU time, whereas CHEMDDM required approximately 1.4 sec. The given execution times do not include the time required for code initialization, preprocessing of the thermochemical data, and input and output. When the number of output stations was increased to 5 (10^{-3}, 10^{-2}, 1, 10, and 20 sec), the difference in computational work required by the codes was even more marked. GCKP87 required 87 steps, 116 functional and 19 Jacobian matrix evaluations, and 0.61 sec CPU time. CHEMDDM, however, required 153 steps, 207 functional and 27 Jacobian evaluations, and 1.5 sec CPU time. This variation of the computational work required by LSODE with the specified value for the first output station has been observed previously (ref. 5). It is caused by the procedure used in LSODE to calculate the first stepsize to be attempted for the problem.

The second example, taken from Hwang (ref. 32), is also a constant temperature problem, but it permits a comparison with the exact solution. It is a simple first-order reversible reaction
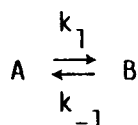
$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

$$\sigma_A(0) = 1000, \quad \sigma_B(0) = 1$$

$$k_1 = 1000, \quad k_{-1} = 1$$

which describes a rapidly changing system. The solution to this problem is

$$\sigma_A(t) = \left[k_{-1}\left(\sigma_A(0) + \sigma_B(0)\right) + \left(k_1\sigma_A(0) - k_{-1}\sigma_B(0)\right)e^{-(k_1+k_{-1})t} \right] \Big/ \left(k_1 + k_{-1}\right)$$

$$\sigma_B(t) = \sigma_A(0) + \sigma_B(0) - \sigma_A(t)$$

Sensitivity coefficients were generated at the same output stations as Hwang (ref. 32) and the results are presented in tables III and IV, together with the exact solutions. The tolerances used for this problem were RTOL = 10^{-6} and ATOL = 10^{-8} to be consistent with Hwang (ref. 32), whose results were generated with RTOL = 10^{-6}. Table III gives the sensitivity coefficients of σ_A with respect to the initial values. In table IV the sensitivity coefficients with respect to the rate constants are presented, along with Hwang's results obtained with a scaled Green's function method (SGFM) (ref. 32). These tables show the excellent agreement between the GCKP87 and exact results. Although the GCKP87 and SGFM results agree well, there are some discrepancies in the SGFM results at early times. In particular, the SGFM sensitivity coefficients with respect to k_{-1} at 1.5×10^{-4} and 1×10^{-3} sec are noticeably inaccurate in comparison to the GCKP87 results. GCKP87 was also significantly more efficient than the SGFM method. To solve for the composition and the sensitivity coefficients of both species with respect to both initial values and both rate constants GCKP87 required approximately 0.3 sec on the IBM 370/3033 computer. In contrast, Hwang (ref. 31) states that the SGFM

8

method required approximately 8 sec on a CDC-CYBER-172 computer. GCKP87 is seen to be significantly faster than the SGFM method even after accounting for the relative slowness of this CDC computer. Hwang (ref. 32) also attempted this problem with a direct method (DM) and gives a CPU time of approximately 7 sec, which is significantly longer than that required by GCKP87. Since no DM results are given in (ref. 32), an accuracy comparison with GCKP87 is precluded.

The last example is also a simple problem for which an analytical solution is known. It is, however, a nonconstant temperature problem involving a first-order irreversible reaction

$$A \xrightarrow{k} B$$
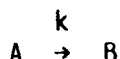
$$k = A\, T^n \exp(-E/RT)$$

$$A = 1, \quad n = 1, \quad E = 0$$

$$\sigma_A(0) = 1, \quad \sigma_B(0) = 0, \quad T(0) = 1000 \text{ K}$$

To solve the problem analytically the following simplifying assumptions were made: (1) constant pressure, adiabatic reaction, and (2) constant and equal specific heats (c_p) for species A and B. The solution is

$$\sigma_A(t) = C\sigma_A(0)e^{-ACt} \Big/ \left[C - \lambda\sigma_A(0)\left(1 - e^{-ACt}\right)\right]$$

$$\sigma_B(t) = \sigma_A(0) + \sigma_B(0) - \sigma_A(t)$$

$$T(t) = T(0) + \lambda\left[\sigma_A(0) - \sigma_A(t)\right]$$

where

$$\lambda = Q_c \Big/ c_p\left[\sigma_A(0) + \sigma_B(0)\right]$$

$$C = T(0) + \lambda\sigma_A(0)$$

where Q_c is the heat of combustion which dictates the temperature rise due to the reaction.

The analytical and computed sensitivity coefficients with respect to A at various times are given in table V. This solution was obtained with values of $Q_c = 5000$ cal/mol and $c_p = 5$ cal/mol K which give a 1000 K temperature rise when reactant A is completely converted to product B. Also presented in this table is the mixture temperature which gives an indication of the extent of the reaction. The agreement between the analytical and the computed results is excellent at all levels of reactedness. In table VI the sensitivity coefficients of the time derivative of σ_A are presented to illustrate the capability of GCKP87 to compute these quantities. The analytical solutions were obtained by differentiating the ODE for σ_A with respect to the rate constant parameters. The solution with respect to A is exact, but those with respect to n and E were obtained by using the computed values for $\partial\sigma_A/\partial n$,

9

$\partial T/\partial n$, $\partial \dot{\sigma}_A/\partial E$, and $\partial T/\partial E$, because these quantities cannot be obtained analytically. The normalization procedure used for A cannot be used for n and E because these parameters can have zero values. The normalization parameters given in table VI ($1/\ln T$ and $-RT$ for n and E, respectively) produce a 1 percent change in k. The normalized sensitivity coefficients with respect to n or E can therefore be interpreted as the percent change in $\dot{\sigma}_A$ due to the change in the parameter n or E that produces a 1 percent change in k. This is analogous to the sensitivity coefficient $\partial \ln \dot{\sigma}_A/\partial \ln A$ which represents the percent change in $\dot{\sigma}_A$ due to a 1 percent change in A. For a constant temperature problem the three normalized sensitivity coefficients are identically equal to one another. Again, the agreement between the analytical results and those generated by GCKP87 is excellent, illustrating the accuracy of this code for sensitivity analysis of nonisothermal combustion kinetic rate equations. Although this problem is simple, selected because the analytical solution exists, GCKP87 has been used successfully on a realistic combustion kinetics problem involving 110 reactions among 36 species (ref. 43).

CONCLUSIONS

An efficient decoupled direct method for calculating the first order sensitivity coefficients of nonisothermal combustion kinetic rate equations has been developed. Sensitivity coefficients of all thermochemical variables and their temporal derivatives with respect to any combination cf initial values of dependent variables and the rate constant parameters of the chemical reactions can be computed. The method was illustrated by application to both constant and varying temperature problems. The computed coefficients agreed well with both analytical solutions and those obtained with other codes and solution methods. The efficiency of the described method compared very favorably with that of other sensitivity analysis techniques.

ACKNOWLEDGMENTS

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TABLE I. - REACTION MECHANISM FOR PROBLEM 1[a]

Reaction	Rate Constant, k_j [b]
(1) $C_2H_6 \rightarrow CH_3 + CH_3$	1.14 (-2)
(2) $CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	1.19 (6)
(3) $C_2H_3 \rightarrow C_2H_4 + H$	1.57 (3)
(4) $H + C_2H_6 \rightarrow H_2 + C_2H_5$	9.72 (8)
(5) $H + H \rightarrow H_2$	6.99 (13)

[a]See reference 37. The initial concentration of C_2H_6 is 5.951 (-6) mol cm^{-3}; all other initial concentrations are zero.

[b]Units are mol, cm, s, and the temperature is 923 K. Numbers in parentheses are powers of 10.

TABLE II. - SENSITIVITY COEFFICIENTS FOR EXAMPLE 1

Species	$\partial \ln \sigma_i / \partial \ln k_1$ at 1.0 sec			$\partial \ln \sigma_i / \partial \ln k_1$ at 20.0 sec		
	[37]	GCKP87	CHEMDDM	[37]	GCKP87	CHEMDDM
C_2H_6	-0.044	-0.043	-0.042	-0.820	-0.800	-0.789
CH_3	1.000	1.000	1.000	1.000	1.000	1.000
CH_4	.976	.977	.977	.643	.650	.655
C_2H_5	.662	.662	.662	-.210	-.191	-.181
C_2H_4	.681	.680	.679	.323	.329	.332
H_2	.602	.602	.601	.221	.227	.230
H	.478	.478	.479	.090	.100	.106

TABLE III. - SENSITIVITY COEFFICIENTS WITH RESPECT TO INITIAL VALUES FOR EXAMPLE 2

[Numbers in parentheses are powers of 10.]

t, sec	$\partial \sigma_A / \partial \sigma_A(0)$		$\partial \sigma_A / \partial \sigma_B(0)$	
	EXACT	GCKP87	EXACT	GCKP87
1.5×10^{-4}	0.861	0.861	1.39(-4)	1.39(-4)
10^{-3}	.368	.368	6.32(-4)	6.32(-4)
10^{-2}	1.04(-3)	1.04(-3)	9.99(-4)	9.99(-4)
1.5×10^{-2}	9.99(-4)	9.99(-4)	9.99(-4)	9.99(-4)
2.0×10^{-2}	9.99(-4)	9.99(-4)	9.99(-4)	9.99(-4)

TABLE IV. – SENSITIVITY COEFFICIENTS WITH RESPECT TO RATE CONSTANTS FOR EXAMPLE σ

[Numbers in parentheses are powers of 10.]

t, sec	$\partial\ln\sigma_A/\partial\ln k_1$			$\partial\ln\sigma_A/\partial\ln k_{-1}$		
	EXACT	GCKP87	[32]	EXACT	GCKP87	[32]
1.5×10^{-4}	-0.150	-0.150	-0.148	1.20(-5)	1.20(-5)	1.35(-5)
10^{-3}	-.999	-.999	-1.03	7.19(-4)	7.19(-4)	8.10(-4)
10^{-2}	-1.390	-1.386	-1.37	.956	.956	.958
1.5×10^{-2}	-1.000	-1.003	-1.00	.999	.999	.999
2.0×10^{-2}	-.999	-.999	-.999	.999	.999	.999

TABLE V. – SENSITIVITY COEFFICIENTS WITH RESPECT TO RATE PARAMETER A FOR EXAMPLE 3

[Numbers in parentheses are powers of 10.]

t, sec	T, K	$\partial\ln\sigma_B/\partial\ln A$		$\partial\ln\sigma_B/\partial\ln A$		$\partial\ln T/\partial\ln A$	
		EXACT	GCKP87	EXACT	GCKP87	EXACT	GCKP87
10^{-6}	1001	-1.001(-3)	-1.001(-3)	1.000	1.000	9.990(-4)	9.990(4)
10^{-5}	1010	-1.010(-2)	-1.010(-2)	1.000	1.000	9.900(-3)	9.899(-3)
10^{-4}	1100	-.110	-.110	.993	.992	9.003(-2)	8.978(-2)
10^{-3}	1761	-1.762	-1.755	.551	.550	.238	.238
10^{-2}	2000	-20.00	-20.09	8.244(-8)	8.150(-8)	4.122(-8)	4.075(-8)

TABLE VI. – SENSITIVITY COEFFICIENTS OF σ_A FOR EXAMPLE 3

t, sec	$\partial\ln\sigma_A/\partial\ln A$		$(\partial\ln\sigma_A/\partial n)/\ln T$		$-RT(\partial\ln\sigma_A/\partial E)$	
	EXACT	GCKP87	EXACT	GCKP87	EXACT	GCKP87
10^{-6}	1.000	1.000	1.000	1.000	1.000	1.000
10^{-5}	1.000	1.000	1.000	1.000	1.000	.996
10^{-4}	.980	.980	.980	.980	.979	.979
10^{-3}	-.523	-.530	-.473	-.482	-.912	-.927
10^{-2}	-19.00	-19.06	-18.98	-18.95	-20.08	-20.05

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16. Abstract

An efficient, decoupled direct method for calculating the first order sensitivity coefficients of homogeneous, batch combustion kinetic rate equations is presented. In this method the ordinary differential equations for the sensitivity coefficients are solved separately from, but sequentially with, those describing the combustion chemistry. The ordinary differential equations for the thermochemical variables are solved using an efficient, implicit method (LSODE) that automatically selects the steplength and order for each solution step. The solution procedure for the sensitivity coefficients maintains accuracy and stability by using exactly the same steplengths and numerical approximations. The method computes sensitivity coefficients with respect to any combination of the initial values of the thermochemical variables and the three rate constant parameters for the chemical reactions. The method is illustrated by application to several simple problems and, where possible, comparisons are made with exact solutions and those obtained by other techniques.

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